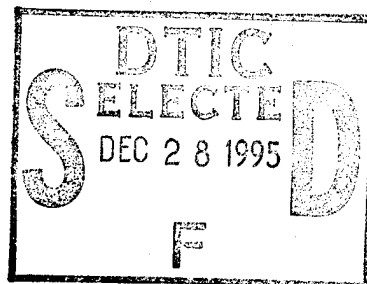
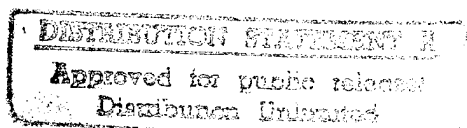


NASA CONTRACTOR REPORT 166329

Long-Term Influence of Physical Aging  
Processes in Epoxy Matrix Composites



Eric S.W. Kong  
Advanced Research and Applications Corporation



DEPARTMENT OF DEFENSE  
PLASTICS TECHNICAL EVALUATION CENTER  
KSCADCOM, DOWEL, IL & BUREAU

CONTRACT NAS2-10480  
February 1981

**NASA**

19951222 039

DTIC QUALITY INSPECTED 1

166329  
NAS 42877

NASA CONTRACTOR REPORT 166329

Long-Term Influence of Physical Aging  
Processes in Epoxy Composites

Eric S.W. Kong

Advanced Research and Applications Corporation  
1223 E. Arques Avenue  
Sunnyvale, California 94086

Prepared for  
Ames Research Center  
under Contract NAS2-10480

*Feb 1981*

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



National Aeronautics and  
Space Administration

Ames Research Center  
Moffett Field, California 94035

# ABSTRACT

Selected mechanical properties of  $(\pm 45)_{4S}$  graphite/epoxy composites have been found to be affected by sub-Tg annealing. Postcured  $(+ 45)_{4S}$  specimens of Thornel 300 graphite/Narmco 5208 epoxy were sub-Tg annealed at 413K (140 C) for ca. 10,  $10^2$ ,  $10^3$ ,  $10^4$  and  $10^5$  min., with a prior quenching from above Tg. The ultimate tensile strength (UTS), strain-to-break ( $\epsilon_B$ ), and toughness of the composite materials were found to decrease as a function of sub-Tg annealing time. No weight loss were observed during the sub-Tg annealing. The time-dependent change in properties can be explained on the basis of physical aging which is related to free volume changes in the non-equilibrium glassy state of network epoxies. The results imply possible changes in composite properties with service time.

## INTRODUCTION

The long-term properties of amorphous, glassy materials, including the crosslinked thermoset of network epoxies, have been demonstrated to change as a function of annealing time at a temperature below the material's glass transition temperature,  $T_g$  (1, 2). This sub- $T_g$  annealing process is typically accompanied by a volume recovery phenomenon known as physical aging (3, 4).

A polymer cooled from above its  $T_g$  is in a non-equilibrium state which possesses excess values in free volume as well as excess values in state functions such as volume and enthalpy. The molecular basis for this non-equilibrium behavior arises from the quenching of free volume into the polymer system due to the inability of the polymer chains to achieve their equilibrium conformation as the temperature of the system is lowered through  $T_g$ . That is, due to the rapidly increasing viscosity as  $T_g$  is approached, the molecules essentially undergo a "log-jam effect" and excess free volume is quenched within the system.

While at a temperature below  $T_g$ , some degree of molecular motion does occur. With time the molecular system does approach the true equilibrium state, i.e., the equilibrium values of volume, enthalpy or other state function variables. Physical aging represents a thermodynamic drive towards the equilibrium glassy state, and the recovery process involves a decrease in free volume as the material ages.

While the non-equilibrium behavior of inorganic glasses has been recognized for many decades, it has only been in the last twenty years or so that the non-equilibrium behavior of organic polymer-glasses has been given some attention. This latter recognition has primarily focused on linear polymeric glasses such as polystyrene (12), poly (ethylene terephthalate)

(12, 13), poly (vinyl acetate), (4, 14) and polycarbonate (15). Only recently has there been some attention given to network or crosslinked glasses such as epoxies (1, 2, 16).

The essence of physical aging in glasses comes forth through striking time-dependent changes in a variety of properties be they mechanical, diffusional or dielectric. Specifically, the general trend is that with sub-T<sub>g</sub> storage time the mechanical behavior shows a trend towards stiffening and embrittlement (1, 2, 15), the diffusional or sorptional behavior decreases with sub-T<sub>g</sub> annealing time for a given penetrant and the dielectric behavior implies a decrease in molecular mobility as noted through the frequency dependence of the dielectric parameters (17, 18).

This report represents the first to recognize the effects of this non-equilibrium behavior in epoxy glasses on the long-term mechanical properties of graphite/epoxy composites. This finding is particularly important in view of the growing applications of graphite/epoxy composites as structural parts in aerospace and automotive industries.

## EXPERIMENTAL

### 1. Materials:

The material chosen for this study was Thornel 300/Narmco 5208 graphite/epoxy composite. This composite is fabricated from prepreg tape manufactured by Narmco Corporation from Union Carbide's Thornel 300 graphite fiber and Narmco Corporation's 5208 epoxy resin. Table 1 gives the physical and mechanical properties of the WYP-30-1/0 (zerotwist) grade of Thornel 300 fiber used in the prepreg (5). The mechanical properties given are those specified by Narmco Corporation, and represent either a minimum or a range for the property value. The actual fiber strength, for instance, probably averages 3000 MPa (435.0 KSi) or higher, with a batch-to-batch variation typically between 2900 and 3300 MPa (420.5 to 478.5 Ksi). (5)

The Narmco 5208 epoxy resin is one of several commercial epoxies based upon the TGDDM-DDS system. That is, the main constituents are tetraglycidyl 4,4'-diaminodiphenyl methane (such as Ciba-Geigy MY-720) crosslinked with 4,4'-diaminodiphenyl sulfone (such as Ciba-Geigy Eporal). The Narmco 5208 system contains about 90 parts-per-hundred (pph) by weight of TGDDM (72.6%), about 24 pph DDS (19.4%), and in addition about 10 pph (8.0%) of glycidyl ether of a bisphenol-A novolac epoxy (such as Celanese SU-8). (6) The chemical structures of these components are shown in Figure 1. Like all epoxy resins, the system can exhibit batch-to-batch variations in the properties of the constituents themselves, and possible additions or deletions of trace components.

Specimens were fabricated by Lockheed Missiles and Space Company, Inc. (Sunnyvale, California), from 12-inch-wide Narmco prepreg tape. Laminates of the arrangement or configuration of  $(\pm 45^\circ)_{4S}$  were fabricated. These were balanced and symmetric 16-ply (16-lamina) specimens having a gauge length of 7.620 cm. (3.000 in.). Their width was typically 1.254 cm. (0.494 in.) and the thickness was typically 0.210 cm. (0.083 in.), giving rise to a cross-sectional area of about  $0.265 \text{ cm}^2$  ( $0.041 \text{ in.}^2$ ). All specimens were about 20.320 cm. (8.000 in.) long with 6.350 cm. (2.500 in.) end-tabs (Figure 2). The end-tabs were used to prevent grip-induced damage during clamping of the specimens by the tensile grips.

The specimens were prepared by the following procedure. Large panels of suitable lamination sequence were prepared from the prepreg tape. These panels were cured in an autoclave held for 0.5 hr. at 408K (135°C) and 2.0 hr at 453K (180°C), under  $6.895 \times 10^5 \text{ Pa}$  (100 Psi or 6.8 atm.) pressure and autoclave vacuum. The percentage of fiber by volume of similar panels were determined to average 64.6%, with a range from 64.3 to 64.8%. Next, Fiberglas<sup>TM</sup> - fabric/epoxy end-tab material was bonded to the panels using a sheet adhesive cured for 1.0 hr at 398K (125°C) at  $3.450 \times 10^5 \text{ Pa}$  (50 Psi or 3.4 atm.). Specimens of the appropriate width were then cut using a dry carborundum cut-off wheel.

## 2. Instrumentation and Test Procedure:

Constant elongation rate tensile tests were performed using a hydraulic-driven tensile test machine manufactured by MTS Systems Corporation, Minneapolis, Minnesota. A strain rate of  $5 \times 10^{-5} \text{ sec}^{-1}$  was used. During deformation, the linear actuator position was monitored and controlled by a linear variable differential transformer (LVDT), while strain was measured using MTS-brand axial and diametral strain-gauge extensometers. The axial extensometer serves to measure the tensile deformation in the direction of loading while the diametral extensometer serves to measure the compressive deformation at  $90^\circ$  to the loading axis due to Poisson's contraction. All tensile tests were performed at 296K ( $23^\circ\text{C}$ ) and in accordance to ASTM D3518-76 (7-9).

The glass transition temperature,  $T_g$ , of Narmco 5208 was determined by differential scanning calorimetry (Perkin-Elmer DSC-2) and by dynamic mechanical analysis (du Pont DMA-981 system). This  $T_g$  was used as the basis for annealing and sub- $T_g$  annealing experiments.

## 3. The Thermal Conditioning Schedule:

Apart from the five as-received composite specimens that were initially tested by the MTS, the rest of the specimens were postcured at 473K ( $200^\circ\text{C}$ ) for 4 hr. in order to totally crosslink the resin. In essence, the post-curing schedule was employed in order to complete the chemical aging process. After the postcuring, specimens were slowly cooled to room temperature at a cooling rate of  $\text{ca. } 0.5^\circ\text{C min}^{-1}$ . Five of these postcured specimens were tested using the MTS. The remainder of the specimens were heated at 433K ( $260^\circ\text{C}$ ) for 20 min. and then immediately quenched into an ice-water bath.



One minute after the quenching, specimens were wiped dry. Five of these quenched specimens were immediately tensile tested. The rest of the quenched specimens were sub-T<sub>g</sub> annealed at 413K (140°C). Time zero for the sub-T<sub>g</sub> annealing or physical aging experiment was defined as the time when an iron-constantan thermocouple adjacent to the specimens reached the temperature of 413K (140°C). The thermocouple was connected to an ice-point junction. Specimens were removed from the 413K (140°C) oven at the time intervals of ca. 10, 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup> and 10<sup>5</sup> min. These air-cooled specimens were stored during the cooling inside a dessicator at 296K (23°C) prior to tensile testing. Five specimens were tested in each decade of aging time.

#### 4. Data Analysis:

The mechanical properties of the composite specimens are defined as follows:

(1) Ultimate tensile strength (UTS):

UTS, also termed ultimate stress, is the stress at which the specimen begins to fail by delamination.

(2) Strain-to-break ( $\epsilon_B$ ):

$\epsilon_B$  is also known as strain-at-failure or elongation-to-failure. It is calculated as

$$\frac{\Delta l}{l_0} \times 100\%$$

where  $\Delta l$  = amount of elongation during the stress - strain experiment  
as measured by the strain-gauge extensometers.

$l_0$  = original length of the specimens.

(3) Toughness:

The static toughness referred to here is different from the dynamic toughness value obtained from impact tests. Toughness is defined here as the area under the stress-strain curve. It is measured by conventional weighing methods and by graphic methods. The former method was employed using a Sartorius electronic balance (Model 1201 MP 2/BCD) which is coupled to an electronic data recording system. The two methods yielded data that were agreeable to each other. A toughness index was calculated as all toughness values (Joules  $\text{CM}^{-3}$ ) were normalized with respect to the value for the  $10^5$  min. aged specimens.

(4) Young's modulus (E):

E is defined as the ratio between stress and strain for the initial linear elastic region of the stress-strain curve.

$$E = \frac{\sigma}{\epsilon} = \frac{\text{stress}}{\text{strain}}$$

(5) Yield Stress ( $\sigma_y$ ):

$\sigma_y$  is defined as the stress value at 0.1% offset strain during the stress-strain experiment (see Figure 3).

## RESULTS AND DISCUSSION

The composite with an epoxy-matrix exhibits mechanical properties which are sensitive to its thermal history. Figure 4 shows that the as-received specimens exhibit by far the greatest degree of toughness. For the as-received materials, UTS averaged  $162.60 \pm 0.76$  MPa (95% confidence level) (Figure 6) whereas  $\epsilon_B$  averaged  $2.44 \pm 0.74\%$  (Figure 8).

Thermal analysis by differential scanning calorimetry on as-received materials indicated that the matrix epoxy was not fully cured: an exotherm was detected during the first scan from room temperature to 573K (300°C). A standard 473K (200°C) 4 hr. postcuring was therefore necessary for the specimens in order to complete all the crosslinking reactions. After the postcuring, differential scanning calorimetry confirmed a fully cured system which exhibit a regular step-function increase in heat capacity at Tg. Tg of Narmco 5208 was found to be between 453K (180°C) and 543K (270°C). This result was confirmed by both dynamic mechanical analysis and differential scanning calorimetry.

Postcuring embrittled the Narmco 5208-matrix composite (Figure 4). After postcuring UTS decreased to  $148.60 \pm 6.41$  MPa (Figure 6) and  $\epsilon_B$  decreased to  $1.04 \pm 0.07\%$  (Figure 8). This postcuring schedule was necessary because we wanted to eliminate the possibility of continuous crosslinking reactions (chemical aging) during our subsequent sub-Tg annealing (physical aging) experiments. It has been demonstrated that chemical aging processes such as continuation of crosslinking reactions would also embrittle polymeric resins (11).

In view of our discussion on the free volume concept, we expect a

quenching from above  $T_g$  would freeze in a relatively large amount of free volume in epoxies. The temperature of 533K (260°C) is well above the onset of the  $T_g$  of Narmco 5208 epoxy. On heating the composite material to 533K (260°C) for 20 min. followed by a quenching to 273K (0°C), we expected to have trapped in a larger amount of free volume compared to the postcured-then-slowly-cooled material. Since more free volume can be interpreted to mean higher chain mobility and shorter molecular relaxation time, we were surprised to find that in the quenched system, the toughness was greatly reduced (Figure 4), i.e., both  $\epsilon_B$  and UTS decreased further compared to the postcured material (see Figures 6, 8 and 10).

We propose to rationalize the observation by a phenomenon known as residual thermal stresses. Residual thermal stresses arise from the fact that graphite and epoxy have different thermal expansion coefficients and a quenching of graphite/epoxy composites would conceivably produce residual stresses. Apparently, the quenching process may produce enough residual stresses to lower the toughness of the composite. In the absence of such residual stresses the free volume concept alone would predict a quenched glass to have larger amount of free volume and hence constitute a less brittle substance (1, 2).

In order to study the effect of physical aging on the graphite/epoxy composites, the freshly quenched materials were then sub- $T_g$  annealed at 413K (140°C). After annealing for only 10 min. at 413K (140°C), the toughness of the composite was restored to a level comparable to that of the 473K (200°C) postcured material (See Figures 4 and 10). It is likely that residual thermal stresses resulted from the quenching were annealed away during this 10 min. thermal aging at 413K (200°C).

Physical aging in the epoxy matrix definitely affects the long-term mechanical properties of the composite. As the material was further sub-T<sub>g</sub> annealed at 413K (140°C) for 100 min., 1254 min., 9907 min and up to 101518 min., the toughness and other ultimate properties continued to decrease (see Figure 5). Figures 7, 9 and 11 show convincingly that the decrease in ultimate properties is proportional to the aging time. By 10<sup>5</sup> min. at 413K (140°C), UTS was down to 100.00 ± 3.30 MPa, a net decrease of 38.5% from the original UTS of the as-received material (Figure 6).  $\epsilon_B$  decreased ca. 73.6% when one compares the as-received materials to the ones aged for 5 decades at 413K (140°C) (Figure 8). Toughness, more drastically, decreased 87.8% as a composite was allowed to go through the thermal treatment described above and aged up to 10<sup>5</sup> min. Both Figure 10 and Table 2 demonstrates this point. For specimens that were aged for 5 decades, we estimate the toughness to have a value of ca. 0.36 Joule cm.<sup>-3</sup>.

No weight loss was observed during the sub-T<sub>g</sub> annealing experiment. Young's modulus estimation indicated insignificant changes during physical aging (Fig. 12 and Table 2). The scatter in the data, however, hamper our analysis significantly. Yield stress analysis did not show any change in properties until the last decade of aging where  $\sigma_y$  dropped approximately 17% (Figure 13 and Table 2).

The inplane shear stress-strain tests reported here have been well demonstrated by other researchers (10) as a reliable test for matrix-dominated properties in composites. For all the selected mechanical properties that we monitored (UTS,  $\epsilon_B$ , static toughness,  $\sigma_y$  and E), their sensitivity to the thermal history was well demonstrated. In particular, the embrittlement

process during the sub-T<sub>g</sub> annealing or physical aging has been clearly observed. This decrease in molecular mobility, which gives rise to an increase in relaxation time and hence a decrease in toughness, can be rationalized as a decrease in free volume in an approach towards the equilibrium glassy state. Further experimental results using techniques such as stress relaxation, fluorescence spectroscopy and dynamic mechanical analysis will most definitely establish the kinetics of this recovery phenomenon and substantiate the effect of physical aging on the durability and reliability of these structural composites.

## CONCLUSION

Mechanical properties of quenched graphite/epoxy composites have been observed to change by thermal aging at sub-T<sub>g</sub> temperatures. The ultimate properties such as UTS and toughness all decreased as a function of sub-T<sub>g</sub> annealing time. The time-dependent change in properties can be explained by a physical aging concept which is based on free volume changes in a non-equilibrium glassy state. The effect of residual thermal stresses, which is likely to be coupled to the physical aging process in this non-equilibrium quenched glass, poses an interesting problem that has to be solved in order to shed more light on this recovery process of physical aging.

TABLE 1

Physical and Mechanical Properties Specified for WYP-30-1/8 (Zero Twist)  
Grade of Thornel 300 Graphite fiber (After Reference 5)

## Physical Properties

filaments/fiber bundle	3000
twist	none
filament density <sup>a</sup>	1.73 Mg/m <sup>3</sup>
filament equivalent diameter <sup>a</sup>	6.9 $\mu$ m

## Mechanical Properties

minimum tensile strength	2660 MPa
average tensile modulus	220 - 240 GPa (Young's modulus)
minimum average strain to failure	1.1% (% strain-to-break)

Notes: <sup>a</sup>from Union Carbide product literature



## FIGURE CAPTIONS

Figure 1:

Chemical structures of the constituents of Narmco 5208 epoxy resin.

Figure 2:

Front view and side view of  $(\pm 45^\circ)_{4S}$  graphite/epoxy specimens showing end-tab reinforcement material.

Figure 3:

Definitions for ultimate tensile strength, strain-to-break and yield stress.

Figure 4:

Comparison of stress-strain curves for  $(\pm 45^\circ)_{4S}$  graphite/epoxy composites of different thermal histories. Error rectangles were drawn to indicate a 95% confidence level for both stress and strain.

Figure 5:

Effect of sub-T<sub>g</sub> annealing at 413K (140°C) on the ultimate properties of graphite/epoxy composites.

Figure 6:

Ultimate tensile strength as a function of composite thermal history.

Figure 7:

Ultimate tensile strength as a function of sub-T<sub>g</sub> annealing time at 413K (140°C).

Figure 8:

Strain-to-break measured by axial extensometer as a function of composite thermal history.

Figure 9:

Strain-to-break measured by axial extensometer as a function of sub-T<sub>g</sub> annealing time at 413K (140°C).

Figure 10:

Normalized toughness index as a function of composite thermal history.

Figure 11:

Normalized toughness index as a function of sub-T<sub>g</sub> annealing time at 413K (140°C).

Figure 12:

Young's modulus of composite as a function of sub-T<sub>g</sub> annealing time.

Figure 13:

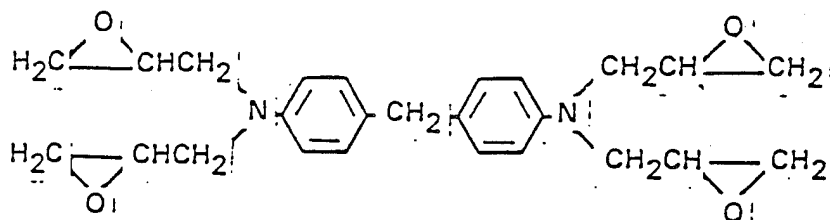
Yield stress of composites as a function of sub-T<sub>g</sub> annealing time.

UTS,  $\epsilon_B$ , Normalized Toughness Index, Young's Modulus and Yield Stress as a  
Function of the Composite Thermal History

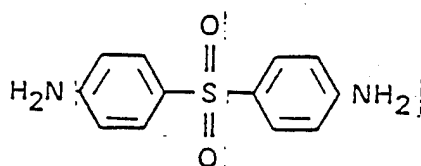
Thermal History	As Received	Postcuring 4 Hr. 473K (200°C)	Annealing 533K (260°C) +Quenching 273K(0°)	Sub-Tg Annealing				
				10 min. (413K) (140°C)	10 <sup>2</sup> min. (413K) (140°C)	10 <sup>3</sup> min. (413K) (140°C)	10 <sup>4</sup> min. (413K) (140°C)	10 <sup>5</sup> (413K) (140°C)
UTS (MPa)	162.60 ±0.76	148.60± 6.41	108.00± 4.71	144.60± 4.25	141.50± 5.71	134.20± 3.60	129.20± 6.76	100.00± 4.60
$\epsilon_B$ (%)	2.44±0.74	1.04±0.10	0.82±0.08	1.08±0.10	1.04±0.07	0.90±0.14	0.84±0.07	0.64±0.08
Toughness [squares counting estimate]	8.23	2.84	1.47	3.08	2.42	1.74	1.66	1.00*
Toughness [weighing method]	8.17	2.75	1.67	3.00	2.50	1.75	1.75	1.00
E (MPa)	20172 ±464	20831 ±2032	19308 ±545	20724 ±776	20278 ±2016	20158 ±319	20420 ±827	19777 ±1756
$\sigma_y$ (MPa)	81.00 ±0.03	119.00 ±5.88	97.40 ±2.91	114.00 ±5.00	113.00 ±5.33	117.00 ±17.79	115.00 ±5.14	95.00 ±7.91

\* Toughness index 1.00 corresponds to 0.36 Joule/cm<sup>3</sup>.

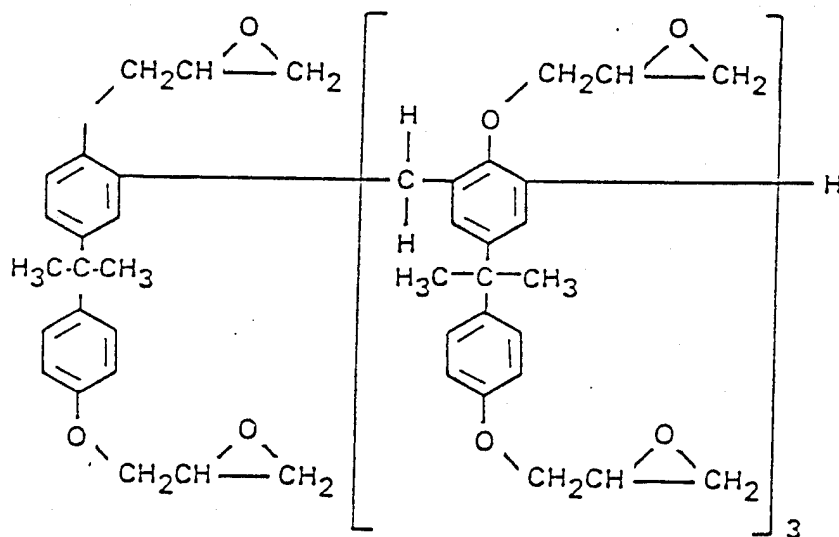
# NARMCO 5208 EPOXY RESIN



TETRAGLYCIDYL 4, 4' DIAMINODIPHENYL METHANE EPOXY (72.6%)



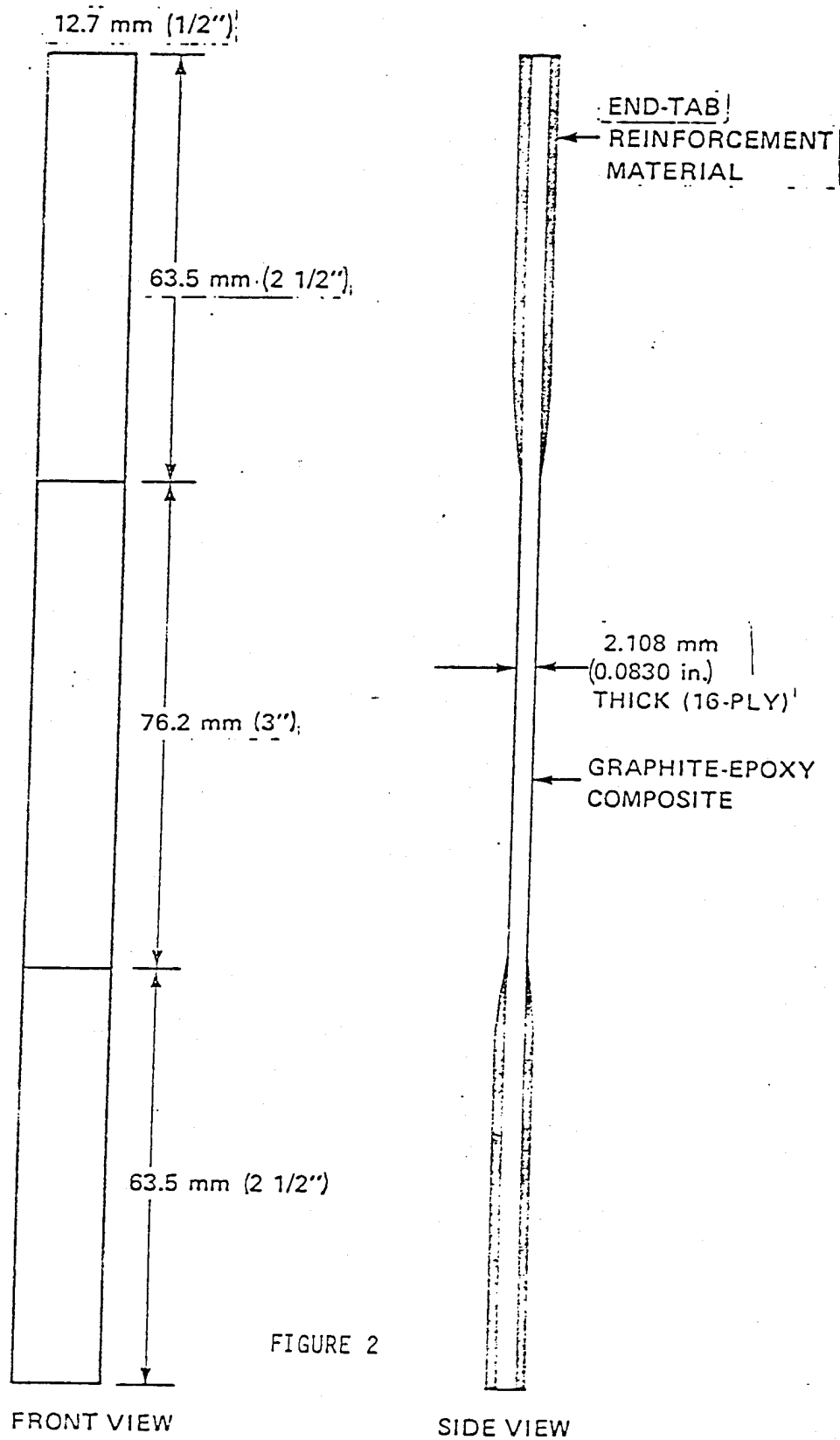
4, 4' DIAMINODIPHENYL SULFONE (19.4%)



GLYCIDYL ETHER OF A BISPHENOL-A NOVOLAC EPOXY (8.0%)

FIGURE 1

FRONT VIEW AND SIDE VIEW OF  
GRAPHITE/EPOXY COMPOSITE SPECIMENS



DEFINITIONS FOR ULTIMATE TENSILE  
STRENGTH, STRAIN-TO-BREAK AND  
YIELD STRESS

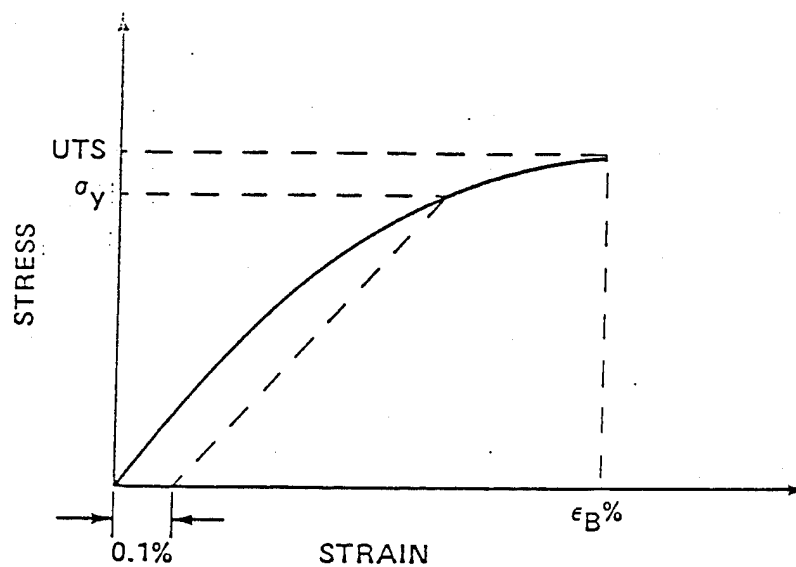


FIGURE 3

## EFFECT OF THERMAL HISTORY ON TENSILE BEHAVIOR

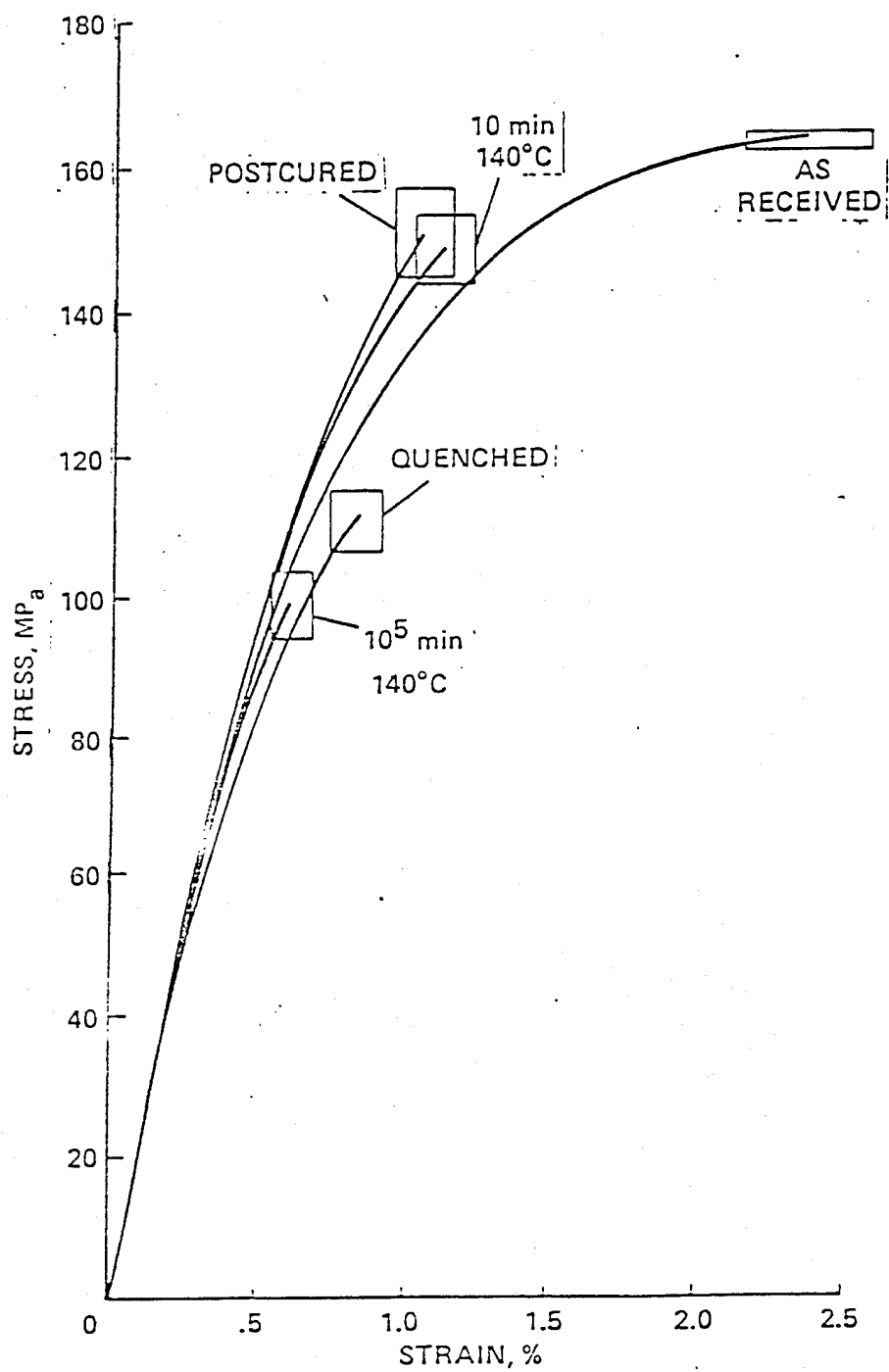


FIGURE 4

# EFFECT OF AGING TIME ON TENSILE BEHAVIOR

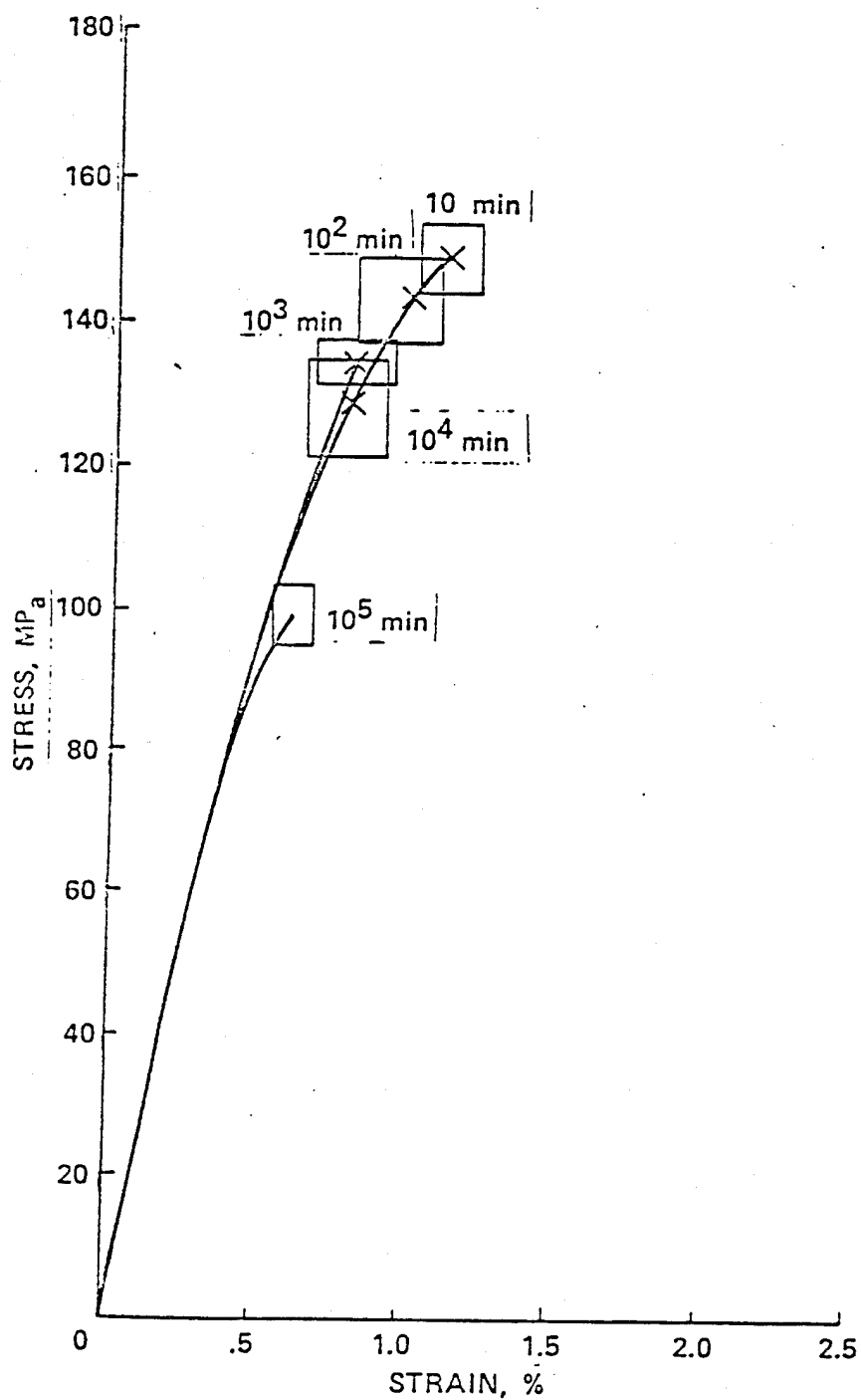


FIGURE 5



# ULTIMATE TENSILE STRENGTH OF GRAPHITE/EPOXY COMPOSITE AS A FUNCTION OF THERMAL HISTORY

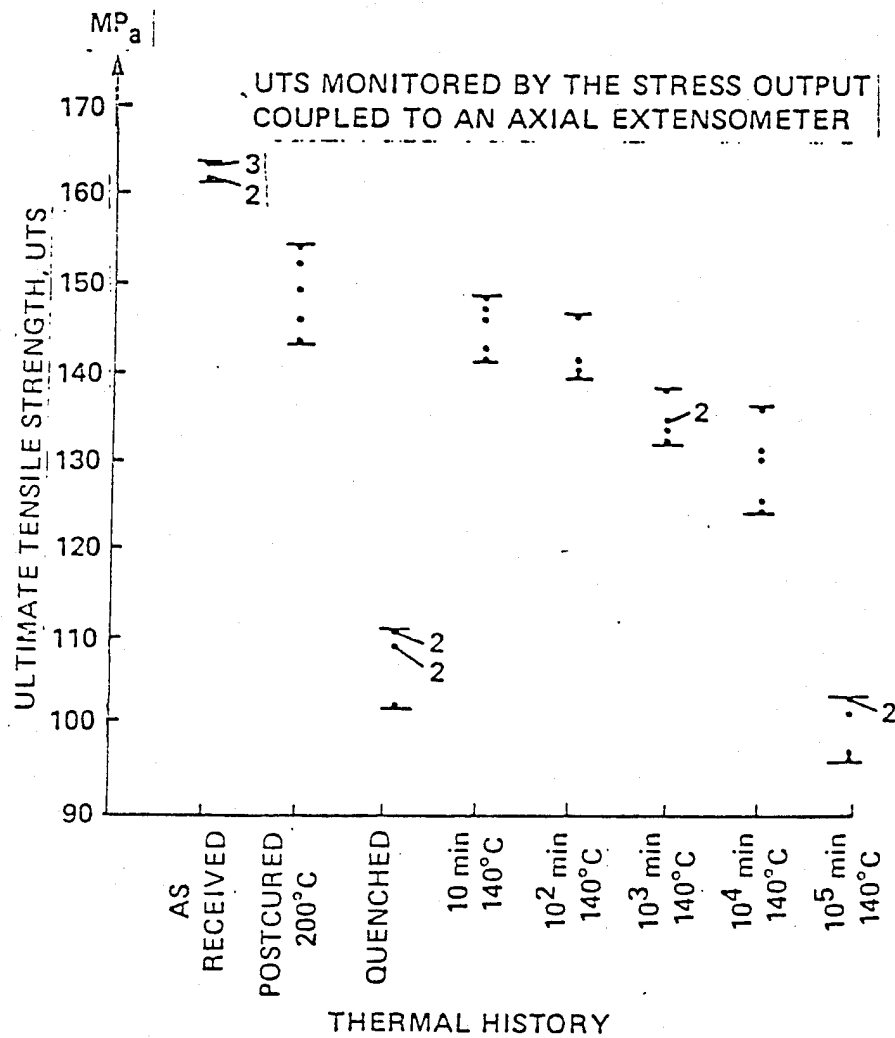


FIGURE 6

ULTIMATE TENSILE STRENGTH OF  
GRAPHITE/EPOXY COMPOSITE AS A  
FUNCTION OF PHYSICAL AGING TIME

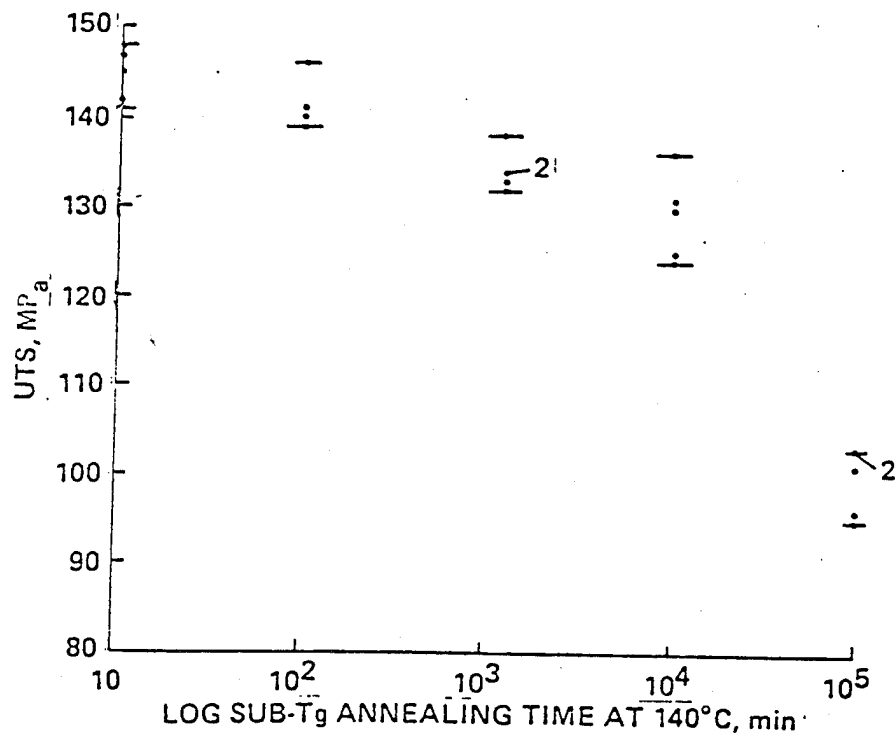


FIGURE 7

# STRAIN-TO-BREAK OF GRAPHITE/EPOXY COMPOSITE AS A FUNCTION OF THERMAL HISTORY

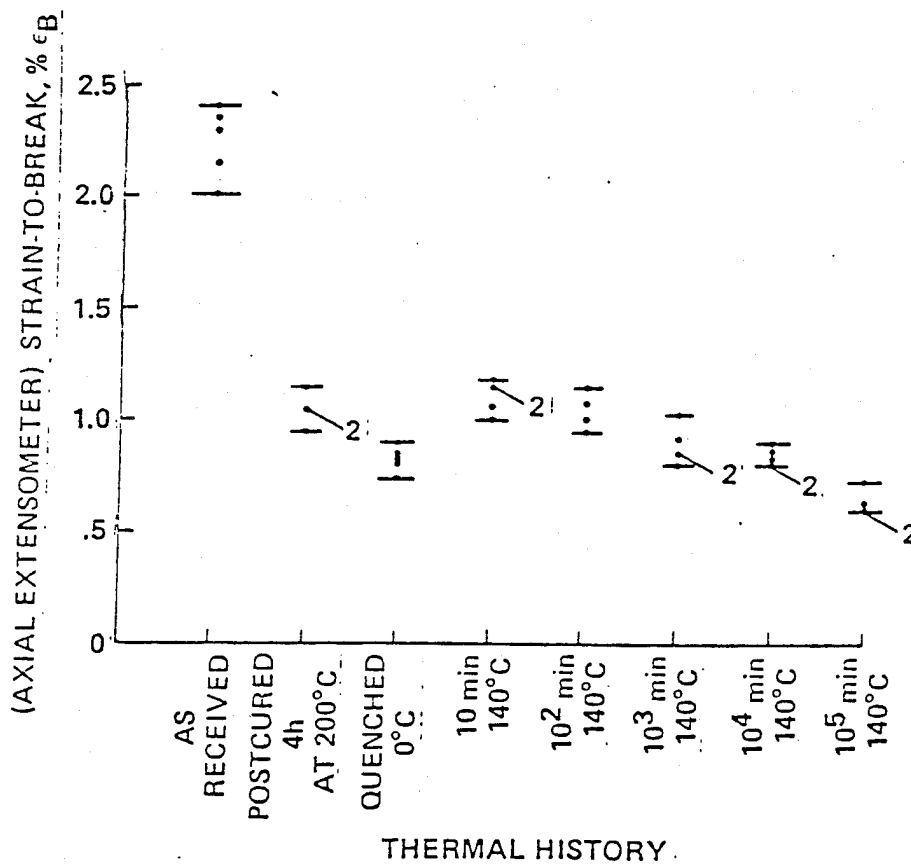


FIGURE 8

STRAIN-TO-BREAK OF GRAPHITE/EPOXY  
COMPOSITE AS A FUNCTION OF  
PHYSICAL AGING TIME

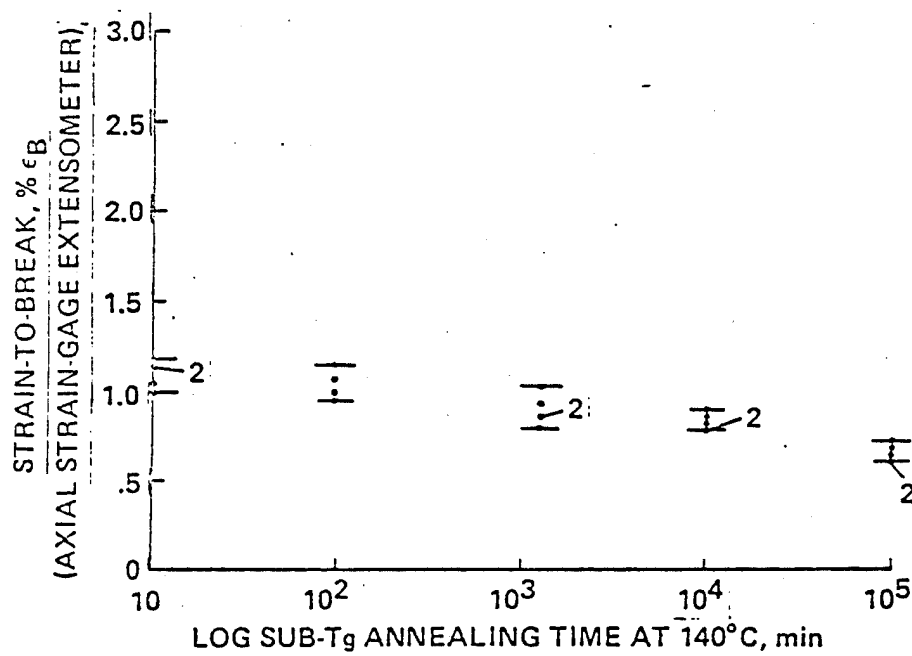


FIGURE 9

# STATIC TOUGHNESS OF GRAPHITE/EPOXY COMPOSITE AS A FUNCTION OF THERMAL HISTORY

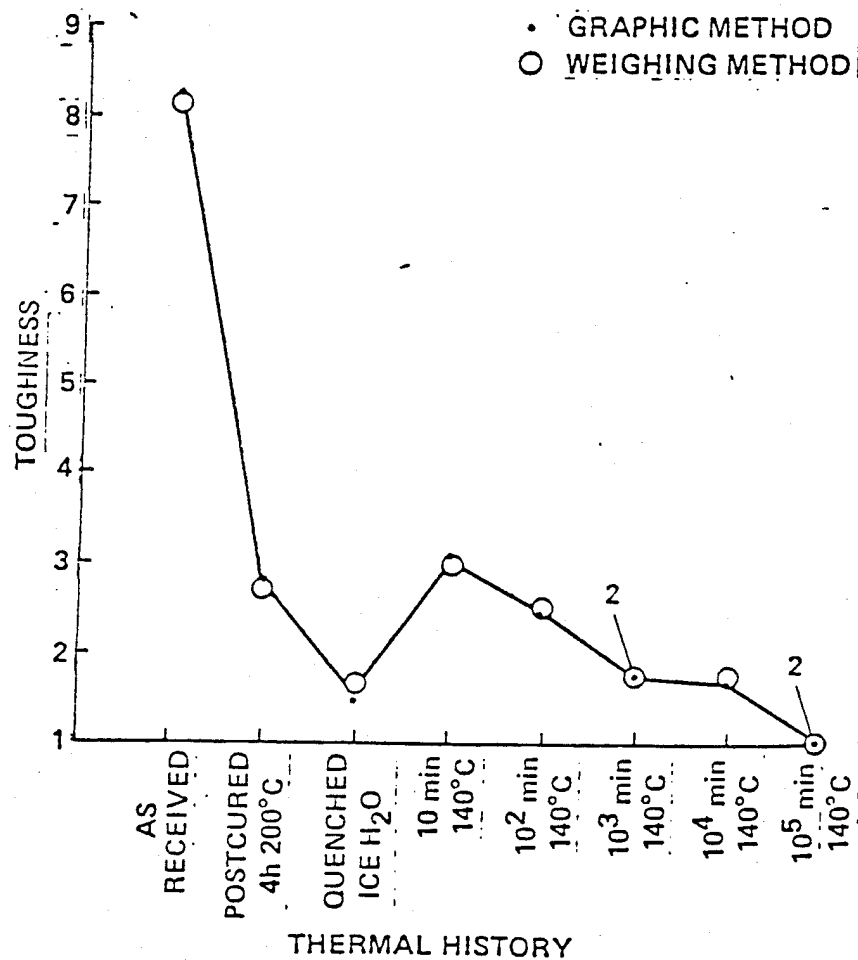


FIGURE 10

# TOUGHNESS OF GRAPHITE/EPOXY COMPOSITES AS A FUNCTION OF PHYSICAL AGING TIME

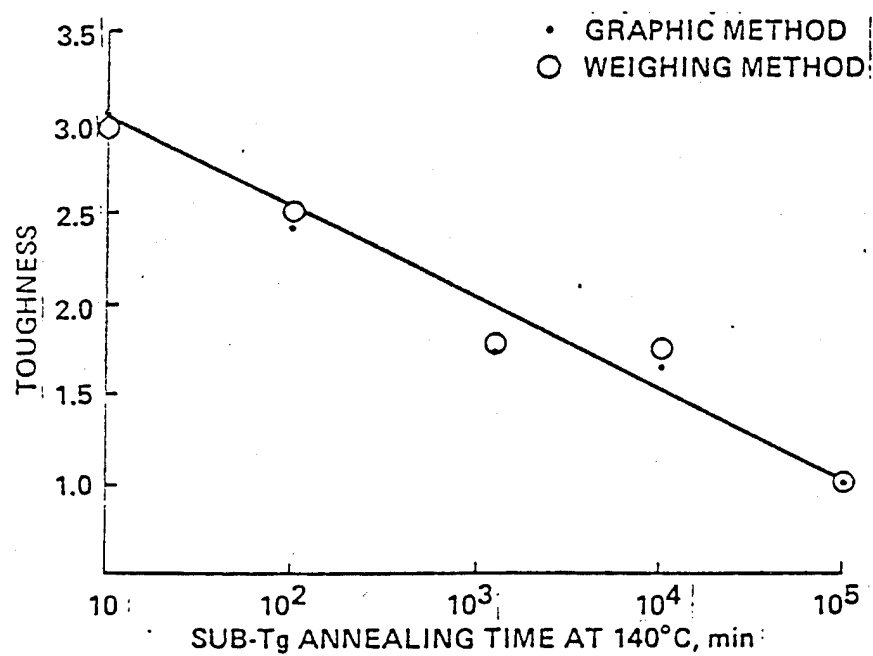


FIGURE 11

# YOUNG'S MODULUS OF GRAPHITE/EPOXY AS A FUNCTION OF PHYSICAL AGING TIME

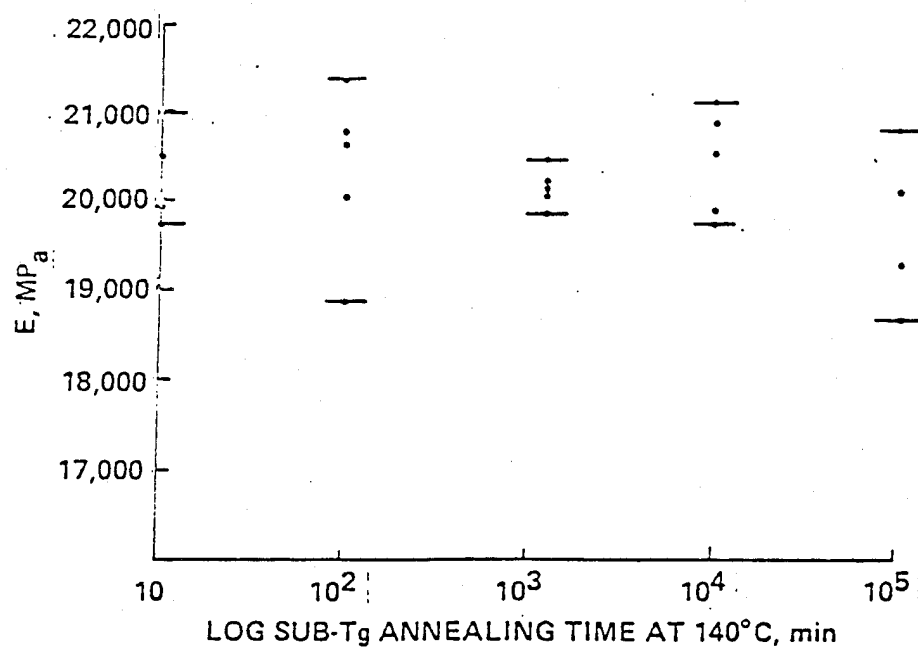


FIGURE 12

YIELD STRESS OF GRAPHITE/EPOXY  
COMPOSITE AS A FUNCTION OF  
AGING TIME

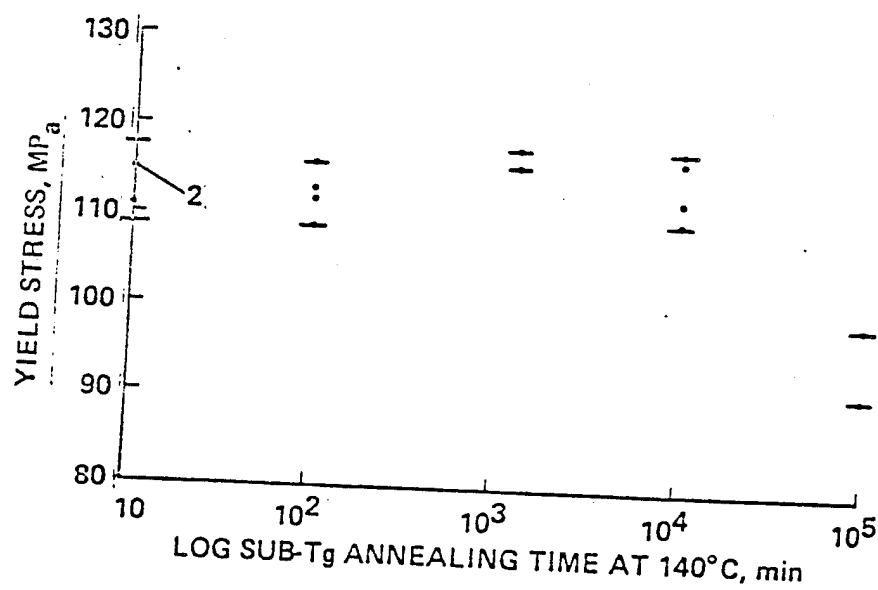


FIGURE 13



## REFERENCES

1. E. S. W. Kong, G. L. Wilkes, J. E. McGrath and H. G. Nelson (1980) NASA Technical memorandum, in press.
2. Z. H. Ophir, J. A. Emerson and G. L. Wilkes (1978), J. Appl. Phys., 49, 5032.
3. L. C. E. Struik (1978), Physical Aging in Amorphous Polymers and Other Materials., Elseveier, Amsterdam, The Netherlands.
4. A. J. Kovacs (1963), Fortschr. Hochpolym. - Forsch., 3, 394.
5. Dale Black, NARMCO Materials, Inc., private communication (1974).
6. Lockheed Missiles and Space Co., Inc., "Exploratory Development of Chemical Quality Assurance and Composition of Epoxy Formualations", Air Force Technical Report AFML - TR - 76 - 112 (1976).
7. "Standard Recommended Practice for Inplane Shear Stress-Strain Response of Unidirectional Reinforced Plastics.", ASTM American National Standard: ANSI/ASTM D 3518-76, pp. 859 - 864 in 1977 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA 19103, USA.
8. B. W. Rosen (1972), J. Composite Materials, 6, 552.
9. G. Terry (1979), Composites, 10, 233.
- 10.. B. D. Agarwal and L. J. Broutman (1980), Analysis and Performance of Fiber Composites. Wiley - Interscience, New York.
11. E. S. W. Kong, G. L. Wilkes (1979), unpublished data on a dental network resin supplied by Johnson and Johnson Company, New Jersey.
12. S. E. B. Petrie (1975), in "Polymeric Materials: Relationships Between Structure and Mecahnical Behavior", Amer. Soc. for Metals, Metals Park, Ohio.
13. M. Tant and G. L. Wilkes (1979), Polym. Preprints, Amer. Chem. Soc., Div. Polym. Chem., 20 (2), 535.
14. A. J. Kovacs (1958), J. Polym. Sci., 30, 131.
15. J. H. Golden, B. L. Hammant and E. A. Hazell (1967), J. Appl. Polym. Sci., 11, 1571.
16. J. Kaiser (1979), Makromol. Chem., 180, 573.
17. G. E. Johnson, S. Matsuoka and H. E. Bair (1978), Preprints, Amer. Chem. Soc., Div. Organ. Coat. Plastics Chem., 38, 350.
18. A. H. Chan and D. R. Paul (1979), Preprints, Amer. Chem. Soc., Div. Organ. Coat. Plastics Chem., 38, 230.

1. Report No. NASA CR-166329		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle LONG-TERM INFLUENCE OF PHYSICAL AGING PROCESSES IN EPOXY MATRIX COMPOSITES				5. Report Date February 1981	
				6. Performing Organization Code	
7. Author(s) Eric S. W. Kong				8. Performing Organization Report No.	
				10. Work Unit No. T-4241	
9. Performing Organization Name and Address Advanced Research and Applications Corporation 1223 E. Arques Avenue Sunnyvale, California 94086				11. Contract or Grant No. NAS2-10480	
				13. Type of Report and Period Covered Contractor report	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				14. Sponsoring Agency Code 505-33-21	
15. Supplementary Notes Ames Technical Monitor: Howard G. Nelson, 230-4, NASA Ames Research Center, Moffett Field, CA 94035 Final Report (415) 965-6137 FTS 448-6137					
16. Abstract  Selected mechanical properties of ( $\pm 45^\circ$ ) <sub>48</sub> graphite/epoxy composites have been found to be affected by sub-T <sub>g</sub> annealing. Postcured specimens of Thornel 300 graphite/Narmco 5208 epoxy were sub-T <sub>g</sub> annealed at 413 K (140 C) for ca. 10, 10 <sup>2</sup> , 10 <sup>3</sup> , 10 <sup>4</sup> , and 10 <sup>5</sup> min., with a prior quenching from above T <sub>g</sub> . The ultimate tensile strength, strain-to-break, and toughness of the composite were found to decrease as a function of sub-T <sub>g</sub> annealing time. The time-dependent change in properties can be explained on the basis of physical aging which is related to free volume changes in the non-equilibrium glassy state of network epoxies. The results imply possible changes in composite properties with service time.					
17. Key Words (Suggested by Author(s)) Time-dependent degradation, Sub-T <sub>g</sub> annealing, mechanical behavior, composite laminate.			18. Distribution Statement  Unlimited - Unclassified  STAR Category - 24		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 44	
				22. Price*	